A structural investigation of heteroleptic lanthanide substituted cyclopentadienyl complexes†‡

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The substituted cyclopentadienyl group 1 transfer agents KCp”, KCp”” and KCp”’ where KCp” = (C₅H₃(SiMe₃)₂-1,3)”, KCp”” = (C₅H₃(SiMe₃)₂-1,2,4)” and KCp”’ = (C₅H₃(Bu₂-1,3)’’)’ were prepared by modification of established procedures and the structure of [K(Cp”’)(THF)]₂ was obtained. KCp” and KCp”’ were reacted with various salts such as [Ln(I)₃(THF)]₂ (Ln = La, Ce) in 2:1 stoichiometries to afford monomeric [La(Cp”’)(I)(THF)]₂ (1a) and the dimeric complexes [La(Cp”’)(µ-I)]₂ (2a), [Ce(Cp”’)(µ-I)]₂ (2b) and [Ce(Cp”’)(µ-I)]₂ (3), KCp”’ was reacted with [Ce(I)₃(THF)]₂ to afford the mono-ring complex [Ce(Cp”’)(µ-I)(THF)]₂ (4), regardless of the stoichiometric ratio of the reagents. Complex 4 was reacted with [K(Ni(SiMe₃)₂)] to yield [Ce(Cp”’)(µ-I)(THF)]₅ (5), [Ce(Cp”’)(µ-I)(Ni(SiMe₃)₂)]₆ (6) and [Ce(Ni(SiMe₃)₂)]₃ by ligand scrambling. Complexes 1–6 have all been structurally authenticated and are variously characterised by other physical methods.

Introduction

Since the first reported synthesis of lanthanide (Ln) cyclopentadienyl (Cp) complexes in the 1950s,1 substituted Cp ligands, CpR, in which up to five ring protons have been replaced by that exhibit unusual Ln oxidation states and bonding modes.3 CpR metallic Ln–TM complexes is alkane elimination.4 It follows that novel heteroleptic [Ln(Cp”’R)₂(X)] (X = halide) complexes that offer significant kinetic stabilisation and are robust with respect to ligand exchange could be useful precursors for supporting novel Ln-element bonding motifs in the future. For the larger lanthanides (La, Ce, Pr, Nd) there is a surprising lack of reports on structurally authenticated [Ln(Cp”’R)₂(X)] complexes,4b,6 and there are very few examples that contain bromide or iodide.9 The employment of the heavier halides is particularly advantageous in salt elimination reactions, where they are less prone to ate complex formation and can offer facile reaction work-ups due to the insolubility of salts such as KI in most organic solvents.5a,b

To target the synthesis of novel [Ln(Cp”’R)₂(I)] complexes of the larger Ln, we focused our attention on a family of established CpR ligands: 1,3-bis(trimethylsilyl)cyclopentadienyl (Cp”, {C₅H₃(SiMe₃)₂-1,3}”), 1,2,4-tris(trimethylsilyl)cyclopentadienyl (Cp”’”, {C₅H₃(SiMe₃)₂-1,2,4}”’) and 1,3-bis(tert-butyl) cyclopentadienyl (Cp”’’’, {C₅H₃(Bu₂-1,3)’’’’}). These ligands have been previously utilised to prepare a variety of homoleptic and heteroleptic La and Ce complexes.3d,b-d,10 Herein we report the reactions of the group 1 ligand transfer agents KCp”, KCp”’ and KCp”’’ in salt metathesis reactions with selected Ln triiodides, leading to the stabilisation and structural authentication of novel monomeric and dimeric [Ln(Cp”’R)₂(I)] (Ln = La, Ce) complexes that are robust towards ligand exchange side-reactions over typical experimental timescales.

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Results and discussion

KCp′′,11 KCp′′′11 and KCp′′12 (Cp′′ = \{C5H4(SiMe3)2-1,3\}3−; Cp′′′ = \{C5H4(SiMe3)2-1,2,4\}3−; Cp′′ = \{C5H4(Bu)2-1,3\}3−) were prepared by slight modifications of published procedures by deprotonation of the pro-ligands with KH or [K(SiMe3)3]. On one occasion, crystals of [K(Cp′)′(THF)]−·THF (1) were obtained, and these were subjected to a single crystal XRD study. The crystals were of poor quality and weakly diffracting, leading to a poor quality dataset. As a result no discussion is given of the metrical parameters although the connectivity is clear-cut (see ESI†). KCp′′′ and KCp′′ were reacted separately in 2:1 stoichiometric ratios with [La(I)3(THF)4] and [Ce(I)3(THF)4] to afford [La(Cp′′′)(µ-I)]2 (2a), [Ce(Cp′′′)(µ-I)]2 (2b) and [Ce(Cp′′)(µ-I)]2 (3) (Scheme 1). The synthesis of [La(Cp′′)(µ-I)]2, was not attempted. Complexes 2a and 2b were obtained in fair crystalline yields but the yield of 3 was significantly lower. It is noteworthy that the syntheses of 2b and 3 from CeI3 were discussed previously by Andersen, although no characterisation data were reported.10

The 1H NMR spectra of 2a and 2b in d6-benzene exhibit resonances for the SiMe3 protons (2a: δ = 0.49 ppm; 2b: δ = −3.23 and 0.29 ppm) and three signals for the Cp′′ ring protons (2a: δ = 7.16, 7.22 and 7.27 ppm; 2b: δ = −7.30, −6.88 and −0.04 ppm). The reason for the difference in the number of SiMe3 group resonances in solution for 2a and 2b is unknown as they have similar solid state structures (see below). A single resonance was observed in the 29Si{1H} NMR spectrum of 2a (δ = −9.69 ppm), but no resonance was observed in the 29Si{1H} NMR spectrum of 2b due to paramagnetic broadening. The 1H NMR spectrum of 3 displays one broad signal for the tert-butyl protons (δ = −1.71 ppm) and three resonances (δ = −5.86 ppm, 0.29 and 1.13 ppm) for the Cp′′ ring protons. Elemental analyses of all three complexes are in good agreement with donor solvent-free [Ln(Cp′′)(µ-I)]2 formulations.

Crystals suitable for X-ray diffraction studies were obtained for 2a, 2b and 3, and their solid state structures were determined (Fig. 1 and 2; see ESI†). Complexes 2a and 2b are structurally analogous, featuring the same open metallocene-type array, so the structure of 2b is depicted here (for a picture of 2a see ESI†). The two compounds display very similar metrical parameters, such as the Ln···Cp centroid [2a: La···Cp centroid = 2.519(7) Å mean; 2b: Ce···Cp centroid = 2.505(3) Å mean] and Ln–I distances [2a: La–I = 3.2128(16) Å mean; 2b: Ce–I = 3.1958(6) Å mean]. These values may be compared to [La(Cp′′)(µ-F)]2, the only other structurally authenticated heteroleptic Cp′′ La or Ce halide-bridged dimer, to the best of our knowledge. In [La(Cp′′)(µ-F)]2 the La···Cp centroid distances [2.548(9) and 2.561(8) Å] are longer than the corresponding distances in 2a and 2b; also the Cp centroid–Ln–Cp centroid angle in [La(Cp′′)(µ-F)]2 [129.42(19)°] is smaller than the analogous angles in 2a [132.8(3)°] and 2b [132.19(10)°]. Such variations are consistent with previous observations on the flexibility of coordinated Cp′′ ligands in Ln chemistry, as they are capable of interlocking with each other in various conformations in order to best accommodate the

![Fig. 1 Molecular structure of 2b with selective atom labelling, with displacement ellipsoids set at the 50% probability level; hydrogen atoms have been omitted for clarity. Symmetry operation to generate equivalent atoms: i = x, y, z. Selected bond distances [Å] and angles [°] for 2b: Ce1–I1 3.1943(6), Ce1–I1–I2 132.19(11), Ce1–Cp centroid–Ce2 129.42(19), Ce1–Cp centroid–Ce2 101.57(16), Ce1–Cp centroid–Ce2 95.78(15).](image)

![Fig. 2 Molecular structure of 3 with selective atom labelling, with displacement ellipsoids set at the 50% probability level; hydrogen atoms have been omitted for clarity. Selected bond distances [Å] and angles [°] for 3: Ce1–I1 3.2238(5), Ce1–I1–I2 132.8(3), Ce2–I1 3.2157(4), Ce2–I2 3.2286(5), Ce1–Cp centroid–Ce2 130.01(19), Ce1–Cp centroid–Ce2 102.218(12), Ce1–Cp centroid–Ce2 101.560(12), Ce1–Cp centroid–Ce2 77.963(11), I1–Ce1–I2 84.422(15), Ce1–I1–Ce2 95.578(15).](image)
space required by co-ligands. This behaviour was reported for a series of heteroleptic Cp⁸ cerium complexes, which exhibited three different Cp⁸ ring orientations in the solid state (Fig. 3A–C). Complexes 2a and 2b adopt orientation C in the solid state and the presence of two SiMe₃ resonances in the ¹H NMR spectra of 2a and 2b (see above) indicates that a low-symmetry orientation is maintained in solution.

On one occasion in an attempted synthesis of 2a we were able to determine the molecular structure of the monomeric THF adduct [La(Cp⁸)ₙ(I)(THF)]. 2a THF (Fig. 4; see ESI†), which resulted from incomplete removal of THF in vacuo prior to recrystallization from toluene. Complex 2a THF displays similar La–Cp_centroid distances to its dimeric counterpart [La(I)–Cp_centroid = 2.539(4) Å mean], however the Cp_centroid–La–Cp_centroid angle in 2a THF [127.97(12)] is smaller. This is due to the absence of a relatively rigid La₂Cl₂ rhomboid in 2a THF, which enables the two Cp⁸ rings to interlock in a staggered conformation (Fig. 3D). To the best of our knowledge, this has not previously been observed for heteroleptic Cp⁸ and Cp⁸ lanthanum and cerium complexes, but it has been reported in Cp⁸ and Cp⁸ U(n) chemistry.¹³

In the solid state 3 exhibits a dimeric structure, with Ce···Cp_centroid distances ranging between 2.510(2) and 2.528(2) Å. These distances are comparable to those observed for [Ce(Cp⁸)₂(I)(μ-Cl)] and [Ce(Cp⁸)₂(μ-H)] (2.538(4) Å mean) [Ce···Cp_centroid distances ranging between 2.510(2) and 2.528(2) Å].¹⁰ Furthermore, the Cp_centroid–Ce–Cp_centroid angles in 3 are relatively small [124.49(7)° and 125.29(7)°], bringing the Cp⁸ rings closer to each other than the Cp⁸ rings in 2a and 2b. These angles are even smaller than those observed in 3a THF, in which a staggered conformation of the Cp⁸ rings was observed in the solid state, yet 3 exhibits a pseudo-ellipsoidal configuration of the Cp⁸ rings (Fig. 3B). It is noteworthy that the ¹H NMR spectrum of 3 exhibits only one signal for the tert-butyl protons (see above), indicating that this high symmetry environment is maintained in solution. In [Ce(Cp⁸)₂(I)(μ-Cl)], the two Cp⁸ rings deviate even further from the ideal parallel sandwich configuration [Cp_centroid–Ce–Cp_centroid = 121.0(2)°]⁴,⁹ demonstrating the potentially large effect of crystal packing interactions on these configurations.¹⁴

An increase in the number of sterically demanding R-groups around a Cp⁸ ring can have significant effects on its coordination to metal centres. It has previously been shown that salt metathesis reactions between group 1 salts of the more sterically encumbered Cp⁸ ligand with LaI₃ afford the mono-ring complex [La(Cp⁸)₂(I)(py)] as the main product,¹⁵ with the bis-Cp⁸ derivative [La(Cp⁸)₂(I)(py)] isolated in poor yields.¹⁶ Germane to this, the mono-ring complex [Ce(C₅Me₅)(I)(THF)] was synthesised from [Ce₄(THF)$_{3}$] and KC₅Me₅, whilst [Li₂(µ₂-OH)(µ₂-C₅Me₅)(µ₂-C₅Me₅)][Cl₄] was isolated when CeCl₃ and Li₂C₅Me₅ were employed as starting materials.¹⁶ Similarly, the reaction of KCp⁸ with [Ce(I)(THF)] resulted in [Ce(Cp⁸)(I)(THF)] (4) regardless of the stoichiometric ratio employed. The ¹H NMR spectrum of 4 exhibits two SiMe₃ proton resonances (δ = -3.74 and 0.27 ppm) and two signals are observed for the Cp⁸ ring protons (δ = -0.03 and 0.76 ppm). The elemental analysis of 4 was consistent with its formulation.

The solid state structure of 4 is depicted in Fig. 5 (see ESI†). Complex 4 exhibits a four-legged piano stool coordination motif, with the two iodides and THF molecules mutually trans with respect to each other [I(1)–Ce(1)–I(2) = 125.53(2)°; O(1)–Ce(1)–O(2) = 149.48(18)°]. The Cp⁸ ring is closer to the cerium centre [Ce(1)–Cp_centroid = 2.495(4) Å] than the Cp⁸ rings in 2b and 3 and this parameter is shorter than the corresponding distance in [La(Cp⁸)(I)(py)], La–Cp_centroid = 2.557 Å.¹⁶ As a mono-ring complex typically has reduced steric crowding around the metal centre compared with the corresponding open metalloocene, the Ce–I bond lengths of 4 [3.0859(7) and 3.1209(6) Å] are shorter than those observed in 2b and 3. These distances are also shorter than those exhibited by [Ce₂C₅Me₅(I)(THF)] [3.2269(12) and 3.1733(12) Å], although this complex contains an additional molecule of THF.¹⁶

In an attempt to prepare a heteroleptic Cp⁸-silylamide cerium complex, “[Ce(Cp⁸)(I)(N(SiMe₃)₂)]”, complex 4 was reacted with one equivalent of [KN(SiMe₃)₂] (Scheme 2). An orange crystalline product was obtained from the reaction mixture, allowing the structural identification of [Ce(Cp⁸)(I)(THF)] (5), which has formed by ligand scrambling (Fig. 6; see ESI†). Complex 5 is
monomeric in the solid state, analogous to the related La Cp”” complex [La(Cp””)[f(py)]. The Ce–O distance in 5 [Ce(1)–O(1) = 2.49(3) Å] is consistent with those measured for 4 (see above) and the Ce–Cp centroid distances of 5 [2.53(2) Å mean] are longer than those in the mono-ring complex 4, as would be expected from the increased steric demands of two Cp”” ligands in 5. The Cp centroid–Ce–Cp centroid angle in 5 [133.77(6)] is comparable to the Cp centroid–La–Cp centroid angle observed for [La(Cp””)[f(py)] [134.50(7)].³ suppression of the Cp centroid–Ce–Cp centroid angles have been previously reported in the literature.⁴,⁵ Further evidence of the steric repulsion in 5 is given by the SiMe₃ substituents, which are pushed away from the cerium centre in comparison to 4 [range of Cp centroid–C–Si angles, 5: 157.4(3)–169.4(4); 4: 168.1(6)–169.9(5)] and are similar to the corresponding angles observed for [La(Cp””)[f(py)] [156.5(4)–167.4(4)].⁶ Complex 5 was further characterised by ¹H NMR spectroscopy, giving a simple spectrum with two resonances for the SiMe₃ protons (δ = 0.30 and 0.99 ppm) and two signals for the Cp”” protons (δ = −5.75 and −5.34 ppm). The elemental analysis of 5 was in good agreement with the proposed formulation.

In order to better understand the ligand scrambling process which led to the formation of 5, several crystals obtained from the third crop of 5 were screened by single crystal XRD. Two additional crystal types were observed: orange needles and dark orange blocks. The needles were identified as [Ce[N(SiMe₃)₂]₂], and the blocks were found to be the heteroleptic complex [Ce(Cp””)[N(SiMe₃)₂]₂] which exhibits similar Ce–N distances [2.35(3) Å mean] to 6 [2.33(3) Å mean]. The Ce–Cp centroid distance in 6 [2.55(1) Å] is comparable to that observed for 4 and all other metrical parameters of 6 are unremarkable. It was not possible to fractionally crystallise analytically pure 6 under the conditions employed due to the similar solubility of [Ce[N(SiMe₃)₂]₂] in hexanes/toluene, therefore no further analytical data were obtained. The global yield of 5 from this reaction was 50%, however, reaction conditions were not optimised as such ligand scrambling mechanisms can be difficult to control. It has been reported that mono-ring C₅Me₅ cerium complexes can undergo ligand scrambling in solution (Scheme 3), and if similar processes are occurring during the synthesis of 5 this would affect the yields of all the products.

The Evans method was employed to determine the room temperature solution magnetic moments of all isolated cerium complexes. The values obtained for 2b (µeff = 2.79 µB), 3 (2.23 µB), 4 (2.41 µB) and 5 (2.22 µB) are in good agreement with the
predicted magnetic moment for a Ce(III) 4f12 F5/2 ground state (1.88–2.75 μB) and previously reported magnetic moments of Ce(III) complexes in the literature (range 1.88–2.75 μB).

Conclusions
We have reported the synthesis and structural characterisation of a novel series of heteroleptic substituted Cp Ln complexes using salt metathesis methodologies. These include bis-substituted CpR Ln dimeric complexes with bridging iodides (2–3) and for the bulky Cp′/′′ ligand we were able to isolate a mono-ring Ce complex 4, as disubstitution was not possible for this ligand under the conditions employed. The monomeric Ce complex 5 was prepared by the reaction of 4 with [KN(SiMe3)2], triggering a ligand scrambling process which gave 5 in fair yield together with the mixed substituted Cp′/′′ silamide Ce complex 6 and [Ce[N(SiMe3)2]3]. Although the yield of 5 is only moderate, it is considerable when compared to the previously reported low-yielding synthesis of the closely related La complex, [La(Cp′/′′)2(THF)]2 (2a).

Solid state characterisation of 2–6 provides in-depth knowledge of the structural features of these systems and this will help us to predict their reactivity profile. In our hands, complexes 2a–b and 5 have not shown any tendency to ligand scramble in both coordinating and non-coordinating solvents over experimental time-scales. As such, we envisage that they will be useful precursors for the preparation and stabilisation of novel La/Ce-element bonding motifs, including the preparation of heterobimetallic species, by salt metathesis methodologies.

Experimental
Materials and methods
All manipulations were carried out using standard Schlenk and glove box techniques under an atmosphere of dry argon. Solvents were dried by refluxing over potassium and were degassed before use. All solvents were stored over potassium mirrors (with the exception of THF, which was stored over activated 4 Å molecular sieves). Deuterated solvents were distilled from potassium, degassed by three freeze-pump-thaw cycles, and stored under argon. KCp′,11 KCp′′,11 KCp′′′,11 [La(I)3(THF)] [La = La, Ce]11 and [KN(SiMe3)2]22 were prepared according to published procedures. KH was obtained as a suspension in mineral oil and was washed three times with hexane and dried in vacuo. 1H, 13C[1H] and 29Si[1H] NMR spectra were recorded on a spectrometer operating at 400.2, 100.6 and 79.5 MHz respectively; chemical shifts are quoted in ppm and are relative to TMS. FTIR spectra were recorded as Nujol mulls in KBr discs on a PerkinElmer Spectrum RX1 spectrometer. Elemental microanalyses were carried out by Stephen Boyer at the Microanalytical Service, London Metropolitan University, UK.

Synthetic procedures

[La(Cp′′)2(μ-I)]2 (2a). A Schlenk flask was charged with KCp′′ (1.74 g, 7 mmol) and [La(I)3(THF)]2 (2.83 g, 3.5 mmol). The flask was cooled to −78 °C and THF (15 ml) was added dropwise with stirring. The yellow reaction mixture was allowed to warm slowly and stirred for 72 h, during which time a suspension formed. The mixture was allowed to settle for 2 hours and the suspension was filtered. The solvent was removed in vacuo (10−2 mbar) and the solid residue extracted with toluene (10 ml). The solution was concentrated to approximately 3 ml and stored at −30 °C to afford 2a as colourless crystals (1.16 g, 48%).

On one occasion crystals of 2a THF were found. Anal. calcd (%) for C44H84La2I2Si8: C, 38.59; H, 6.18. Found: C, 38.47; H, 6.28.

1H NMR (δd-benzene, 298 K): δ = 0.49 (s, 72H, Si(CH3)3), 7.16 (m, 4H, Cp′−CH), 7.22 (m, 4H, Cp′′−CH), 7.27 (m, 4H, Cp′′′−CH), 11C[1H] NMR (δd-benzene, 298 K): δ = 1.51 (s, Si(CH3)3), 123.32 (Cp′−C), 126.27 (Cp′′−CH), 132.28 (Cp′′′−CH).

29Si[1H] NMR (δd-benzene, 298 K): δ = −9.69 (s, Si(CH3)3). FTIR (Nujol, cm−1): ν = 1318 (m), 1249 (br s), 1077 (s), 919 (s), 833 (br s), 752 (s), 690 (m).

[Ce(Cp′′)2(μ-I)]2 (2b). A Schlenk flask was charged with KCp′′ (4.97 g, 20 mmol) and [Ce(I)3(THF)]2 (8.01 g, 10 mmol). The flask was cooled to −30 °C and THF (20 ml) was added dropwise with stirring. The reaction mixture was allowed to slowly warm to room temperature and then stirred for a further 16 hours. The mixture was allowed to settle for 2 hours and the suspension was filtered, giving a clear yellow solution. Volatiles were removed in vacuo (10−2 mbar), affording a bright pink solid. Recrystallisation from toluene (30 ml) afforded 2b as a crystalline product (2.85 g, 42%).

1H NMR (δd-benzene, 298 K): δ = −7.30 (s, 4H, Cp′−CH), −6.88 (s, 4H, Cp′′−CH), −3.23 (s, 36H, Si(CH3)3), −0.04 (s, 4H, Cp′′′−CH), 0.29 (s, 36H, Si(CH3)3). Anal. calcd (%) for C42H45Ce2I2Si8: C, 38.39; H, 6.23. Found (%): C, 38.52; H, 6.18. μeff (Evans method, 298 K, δd-benzene): 2.79 μB. FTIR (Nujol, cm−1): ν = 1260 (s), 1078 (br s), 919 (m), 836 (br m), 800 (br m).
[Ce(Cp”)(µ-I)]₂ (3). A Schlenk flask was charged with KCp” (0.82 g, 4 mmol) and [Ce(µ-I)(THF)]₂ (1.62 g, 2 mmol). The flask was cooled to −78 °C and THF (15 ml) was added dropwise with stirring. The yellow reaction mixture was allowed to slowly warm to room temperature and then stirred for a further 16 hours. The mixture was allowed to settle for 2 hours and the suspension was filtered. Volatiles were removed in vacuo (10−2 mbar), affording a bright orange solid. The solid residue was extracted with toluene (8 ml) and stored at room temperature, affording 3 as an orange crystalline product (0.30 g, 24%). ¹H NMR (δ, benzene, 298 K): δ = −5.86 (br s, 6H, Cp”-CH₃), −1.71 (br s, 72H, Si(CH₃)₃), 0.29 (s, 2H, Cp”-CH), 1.13 (s, 4H, 4, 5-H). Anal calcld (%) for C₂₃H₄₆CeISi₆: C, 42.64; H, 7.27. Found: C, 42.72; H, 7.38.

A THF (20 ml) solution of [KN(SiMe₃)₂] (1.00 g, 5 mmol) was added dropwise to a THF (15 ml) slurry of [Ce(µ-I)(THF)]₂ (4.05 g, 5 mmol) at −4 °C with stirring. A colour change to yellow with a white precipitate was observed, and the mixture was slowly warmed to room temperature and stirred for 72 hours. Volatiles were removed in vacuo, yielding a bright yellow powder. The solid was extracted with hexane (20 ml) and volatiles were removed in vacuo (10−2 mbar), affording 4 as a yellow powder (2.39 g, 58%). A small crop of crystals were grown from hexanes (2 ml) at −25 °C. ¹H NMR (δ, benzene, 298 K): δ = −3.74 (s, 18H, Si(CH₃)₃), −0.03 (s, 1H, Cp”-CH), 0.27 (s, 1H, Cp”-CH), 0.76 (s, 9H, Si(CH₃)₃), 2.25 (br m, 16H, THF). Anal calcld (%) for C₂₃H₄₆CeI₂O₂Si₃: C, 32.23; H, 5.53. Found (%): C, 32.08; H, 5.61. (Evans method, 298 K, δ, benzene): 2.21 µµ, FTIR (Nujol, cm⁻¹): ν = 1250 (m), 1201 (w), 1165 (m), 1089 (w), 1054 (br m), 1021 (m), 935 (m), 837 (br s), 753 (m).

A Schlenk flask was charged with KCp tt (1.60 g, 5 mmol) was added dropwise to a THF (15 ml) slurry of [Ce(Cp tt)₂(O)₂] (5) and [Ce(Cp tt)(µ-I)(THF)] (5) and [Ce(Cp tt)(µ-I)(THF)] (6). A toluene (20 ml) solution of [KN(SiMe₃)₂] (1.00 g, 5 mmol) was added dropwise to a toluene (20 ml) solution of 4 (4.10 g, 5 mmol) at −20 °C with stirring. The reaction mixture was warmed to room temperature and stirred for 16 hours, forming a dark orange mixture with a white precipitate. The suspension was filtered, the solution concentrated to 5 ml and cooled to 4 °C, yielding orange crystals of 5. More crops of 5 were obtained from the supernatant liquid of the first crystallisation (2.36 g, 50%). From the third recrystallisation several crystals with different morphologies were observed. These were identified as [Ce(N(SiMe₃)₃)₃] (orange needles) and 6 (orange blocks) via single crystal X-ray studies. Data for 5: ¹H NMR (δ, benzene, 298 K) δ = −5.75 (s, 2H, Cp”-CH), −5.34 (br s, 2H, Cp”-CH), 0.30 (s, 36H, Si(CH₃)₃), 0.90 (s, 18H, Si(CH₃)₃). (Evans method, 298 K, δ, benzene): 2.22 µµ. Anal calcld (%) for C₂₃H₄₆CeI₂Si₆: C, 44.26; H, 7.27. Found: C, 44.27; H, 7.38 (%). FTIR (Nujol, cm⁻¹): ν = 1249 (s), 1090 (s), 986 (s), 935 (m), 837 (br s), 753 (m).

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### Notes and references


